# U.S. Department of Energy's Initiatives for Proliferation Prevention in Russia: Results of Radioactive Liquid Waste Treatment Project, Year 1

Yury Pokhitonov, Vladislav Kamachev
V.G. Khlopin Radium Institute, St. Petersburg, Russia

Dennis Kelley
Pacific Nuclear Solutions, Indianapolis, Indiana

## ABSTRACT

The objective of the project is to engage weapons scientists with training and research programs at selected nuclear sites in Russia and apply high technology polymers to immobilize legacy ILW and HLW liquids that have posed environmental challenges over the years. One compelling advantage of the project is that V.G. Khlopin Radium Institute and Pacific Nuclear Solutions have been engaged for seven years of applied research to validate the performance and effectiveness of the polymer technology for use with radioactive liquids. With conclusive results of the research work on sixty active and simulant waste streams, the project can focus on actual applications of the technology at Ozersk (MAYAK), Seversk (SCC) and Zheleznogorsk (MCC) rather than on research.

The long term objective of the project is find viable waste management solutions for serious radioactive and chemical contamination that has existed in Russia and the U.S. for several decades. The polymer technologies may be applied to all radioactive liquid. This paper summarizes the experimental work of the immobilization process and data definition of the most effective polymer compositions in addition to determining the optimum polymer to liquid ratios for economic considerations.

## INTRODUCTION

The idea of using polymer materials for liquid radwaste treatment first appeared in the 1950's. Numerous publications during last several decades described the advantages and disadvantages of polymer; however, in the 1990's the interest in polymers declined considerably due to two factors: firstly, polymers created in the 1980's were thought to degrade over time from the effects of radiation and secondly, mixing of additives in the treatment process caused health concerns for workers. Additional concerns were volumetric increase of the waste form and leachability. Other technological advances on an industrial scale such as cementation, and vitrification led to new options for radwaste treatment. The use of polymer technology in radwaste treatment has been described in a reasonably detailed IAEA Technical report [1].

On the other hand, demands for more effective treatment technologies has emerged because of the extraordinarily large amounts of organic and aqueous waste that exists worldwide which cannot be treated by cementation and glass. A new technology, a 3$^{rd}$ generation elastomeric polymer created by Nochar® Corp., USA [2], is designed for use in the nuclear environment. The polymers absorb organics, solvents, other hydrocarbons and all aqueous waste with a mixture or "formula" of high tech polymers that can be combined to address the specific characteristics of combined waste liquids. The polymers can be applied to immobilize the organic / aqueous liquid into a soft sponge rubber-like material or a granule-like material which can be disposed of directly in containers,

incinerated or incorporated into a grouted matrix depending upon the governing requirements of the overseeing state or nation. [3,4,5]

Extensive, high dose Cobalt 60, gamma irradiation testing has been conducted in Russia, China and the USA and conclusive results indicate that the polymers will not degrade over hundreds of years. Given the success of the polymer technology at nuclear sites worldwide during the last ten years, the U.S. Department of Energy approved a three-year project entitled "Solidification Technologies for Radioactive and Chemical Liquid Waste Treatment" under its Initiatives for Proliferation Prevention Program in January, 2009. The initial focus of the project concentrates on four sites under the supervision of the Russian State Atomic Energy Corporation (ROSATOM). The project managers are V.G. Khlopin Radium Institute, Russia, and Pacific Nuclear Solutions, USA with management administration and oversight provided by Argonne National Laboratory and the International Science and Technology Center (ISTC), Moscow.

This paper will describe some of the experiments and results of one of the most problematic waste streams in Russia, aqueous solutions. The experiments using stimulants and active waste streams focus on absorption, weight loss / evaporation, and issues with cementation and a final waste form suitable for final storage. These tests are required for the polymer certification by Russian regulators. Although extensive irradiation testing was also performed in 2009, those results are not shared in this paper; however, they are available from the authors. [6,7] Additional work is underway to analyze the cost savings of treatment and disposal using the polymer technology.

## RESULTS OF EXPERIMENTS

One of the most widely used and inexpensive methods for aqueous radioactive solution solidification (LLW and ILW category) is encapsulation in a cement matrix.
The cementation technique does not require any specially designed equipment or expensive reagents for stability. However, it is not possible to use this technique for direct acid / aqueous solidification. It is a customary practice to carry out preliminary neutralization of acidic solutions in order to achieve successful encapsulation.

Although cementation is a popular form of waste treatment in many countries, it results in large amounts of waste that is moved into a repository which requires additional designed equipment. Given the volumetric increase of cemented waste forms, cement creates high costs for final storage. The advantage of polymer materials is its ability to solidify waste streams directly with high content of acidity and salts with little or no volumetric increase.

The first phase of the experiments was carried out by the Radiochemistry Department of the Khlopin Radium Institute (Gatchina) on simulated nitric acid ($HNO_3$) and real technological (active) solutions. Examples of these experiments and the results are shown in Tables 1 & 2.

**Table 1**
Polymer # 960 was applied to the aqueous liquids. Samples of polymers were prepared in advance and were added and mixed into the solution.

| № | Conditions of solidification | | | Results |
|---|---|---|---|---|
| | Weight of polymer, g | Volume of solution, $sm^3$ | Amount of solution | |
| 1 | 7,1 | 55 | 0,5 M $HNO_3$ | After 15-17 hours, no free liquid present |
| 2 | 6 | 50 | 0,5 M $HNO_3$ | After 1 hour jelly-like mobile mass |

| | | | | |
|---|---|---|---|---|
| 3 | 12 | 50 | 0,5 M $HNO_3$ | After 7-10 minutes, no free liquid present<br>There is excess of polymer at the bottom |
| 4 | 3 | 25 | $H_2O$ | After 7-10 minutes, no free liquid present<br>There is excess of polymer at the bottom |
| 5 | 6 | 25 | $H_2O$ | After 7-10 minutes, no free liquid present<br>There is excess of polymer at the bottom |
| 6 | 3 | 25 | 5 M $HNO_3$ | After 1 hour – jelly-like, weakly mobile mass. Some free liquid is present |
| 7 | 6 | 25 | 5 M $HNO_3$ | After 1 hour, no free liquid present<br>There is excess of polymer at the bottom |
| 8 | 3 | 25 | 0,5 M $HNO_3$ | After 1 hour – jelly-like mass, some free liquid present |
| 9 | 15 | 50 | 0,5 M $HNO_3$ | After 7-10 minutes in upper part of the beaker mobile jelly-like mass is present. After 20- 25 minutes, the sample looks like jelly mass. No free liquid present |

Three months of analysis and evaluation of the radwaste types indicate that the test samples are successfully solidified and with no volumetric increase. The final examination was conducted after three months aging and all samples were exposed to air at room temperature. The appreciable reduction of volume through evaporation was noted. The appearance of the sample after solidification and aging over three months is presented in Figure 1.

Normal lab testing would be conducted on the basis of weight of the polymer to weight of the liquid in order to achieve exact solidification results. However, in this case testing was conducted on the basis of weight of polymer to liquid volume. This is a new approach and considers real conditions of radwaste treatment in underground and above ground closed vessels.

**A** **B**

**Fig. 1** (A) Appearance of specimen after solidification (B) After aging in air at room temperature

Besides experiments on $HNO_3$ solutions solidification, active solutions were tested and solidified as shown in Table 2.

**Table 2**
Results of experiments on the solidification of real technological solutions. (Specific activity of these solutions was in the range $-10^{-2}$ - 5 Cu/l.)

| # | Characteristic (composition) of wastes | Conditions of solidification. | | | Results |
|---|---|---|---|---|---|
| | | Volume of waste used, ml | Amount of polymer used, g | | |
| | | | # 960 | # 910 | |
| 4232 | Sludge residue from the bottom of the apparatus (aqueous phase).U–80 g., $NaNO_3$ ~ –200 g, $HNO_3$-0,8 M/l | 6 | 8 | 0,5 | Successfully solidified |
| 4231 | Sludge residue from the top of the apparatus (occurrence of organic phase is probable).U–80 g., $NaNO_3$ ~ –200 g, $HNO_3$-0,8 M/l. Very thick black liquid. | 6 | 8 | 0,5 | Successfully solidified |
| 4237 | LL decontaminating solution with low amounts of organic substances. U–153 g/l, $NaNO_3$ ~ –100-150 g, $HNO_3$-2,5 M/l. | 12 | 8 | 0,5 | Successfully solidified |
| 4238 | LL decontaminating solution with low amounts of organic substances. U–153 g/l, $NaNO_3$ ~ –100-150 g, $HNO_3$-2,5 M/l. | 20 | 4 | 2 | Successfully solidified |
| 4125 | U–20 g, $NaNO_3$ –40 g, $HNO_3$-1,2 M/l. There was a precipitate in the solution. | 15 | 16 | 0,5 | Successfully solidified |
| 4283 | Uranium re-extracts. U–70 g, $HNO_3$-0,07 M/l. | 20 | 4 | 1 | Successfully solidified. |

Polymer # 910 was combined with # 960 in order to capture the organic content of the solution. In all cases after several hours no free liquid was present.
In accordance with the data obtained a conclusion can be made that the polymers have a versatile effect and are capable of solidifying aqueous solutions of various acidities and specific activities, suspensions and sludge of different compositions.

Simultaneously, experiments were carried out to determine the leach rate of radionuclides from the solidification. The appearance of the samples after water has been added to estimate leach rate of radionuclide is presented in Figure 2.


**Fig. 2** Appearance of the specimen after solidification and after water has been added. (Low Level decontaminating solutions, # # 4237, 4238 in Table. 2.)

Considering the results obtained in the test program, the next set of experiments were established to evaluate the conditions which affect the characteristics of the solidified final products, ie., evaporation and water absorption (the relationship between the mass of polymer and the mass of liquid phase; composition of solution; time of aging after simulated solution immobilization).

It is interesting to obtain data on the volume of water that can be absorbed after aging in the open air (evaporation) and determine the polymer's capacity to absorb more solution when added to the first solidified sample. This is an important outcome because the chemical stability of substances intended for radwaste disposal is first and foremost studied for its reaction with water.

The experiments on solidification have been carried out in polypropylene or Teflon cups. The total mass in individual experiment (solution + polymer) was 50 g. In all cases after adding additional solution to the solidified sample, no free liquid was present after a 7-10 minute period. Samples were a jelly-like mass as the absorption capacity of the polymers was extended. After aging in air the specimen's surface did not indicate any volumetric increase. Some specimens cracked and became separate pieces (Fig. 3, 4). In Table 3, the data of weight loss (evaporation) after solidification and aging in air over a 21 day period are presented. The same table shows the amount of water absorbed after air storage.

After three weeks aging on the air specimens were weighed and the part of specimen were put into polypropylene cup and the cup was filled with distillated water on the basis of 50 ml to 1g solid phase. After one day an attempt was made to remove water and measure the volume of free liquid. In an overwhelming majority of experiments water separation was not possible because all water had been absorbed by the sample (Table 3). The polymer technology is irreversible as the liquid is permanently immobilized in the polymer matrix.

**Table 3.**
Results of experiments on solidification simulated solutions. (Polymer # 960.)

| ## | Relationship between the mass of polymer and the mass of liquid phase, $M_p$:$M_l$ | Loss of weight after aging samples, during 21 days, % | Amount of water absorbed by samples after solidification during 21 days. (weight of water /1 gram solidificated sample) |
|---|---|---|---|
| | | $H_2O$ | |
| 1 | 2:1 | 33,7 | All water has been absorbed by the sample |
| 2 | 1:2 | 66,47 | All water has been absorbed by the sample |
| 3 | 1:5 | 83,26 | All water has been absorbed by the sample |
| | | NaOH, 0,1M | |
| 4 | 1:1 | 53,91 | All water has been absorbed by the sample |
| 5 | 1:2 | 66,25 | All water has been absorbed by the sample |
| 6 | 1:5 | 82,76 | All water has been absorbed by the sample |
| | | $HNO_3$, 0,1M | |
| 7 | 1:1 | 49,73 | All water has been absorbed by the sample |
| 8 | 1:2 | 66,34 | All water has been absorbed by the sample |
| 9 | 1:5 | 82,88 | All water has been absorbed by the sample |
| | | $HNO_3$, 0,5M | |
| 10 | 2:1 | 32,49 | All water has been absorbed by the sample |
| 11 | 1:2 | 65,41 | All water has been absorbed by the sample |
| 12 | 1:5 | 81,72 | 24,5 |
| | | $HNO_3$, 1,0M | |
| 13 | 1:1 | 48,34 | All water has been absorbed by the sample |
| 14 | 1:2 | 64,06 | All water has been absorbed by the sample |
| 15 | 1:5 | 79,55 | 3,8 |
| | | $HNO_3$ 0,5 M + $NaNO_3$100 g/l | |
| 16 | 1:1 | 44,66 | All water has been absorbed by the sample |
| 17 | 1:2 | 60,13 | All water has been absorbed by the sample |
| 18 | 1:5 | 74,19 | 18,8 |

**Fig. 3** The appearance of solidified specimen after water has been added.
(Solution $HNO_3$, 0,5M, # 15 in Table. 3.)

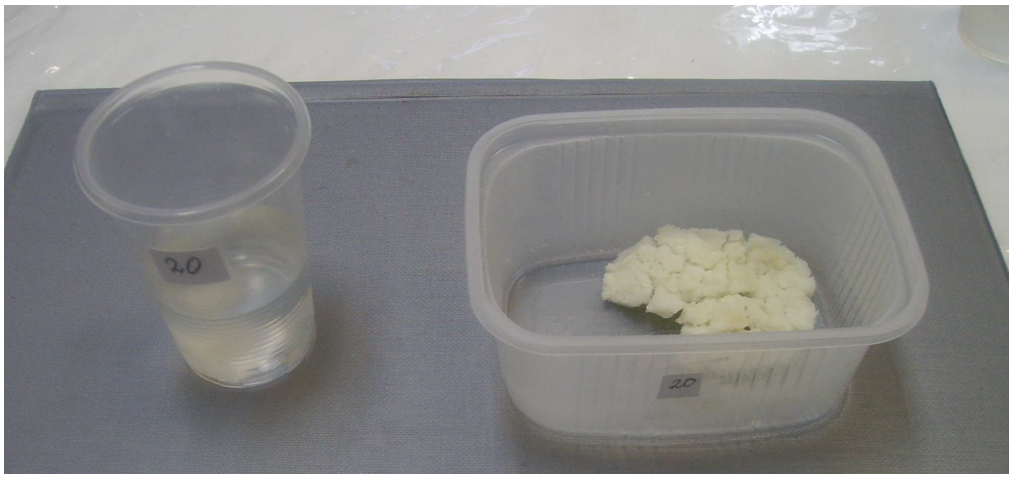

**Fig. 4** The appearance of solidified specimen after water has been added.
(Solution $HNO_3$, 1,0M, # 20 in Table. 3.)

It is an abnormal parallel that with obvious merits (possibility to solidify of all kinds solutions) of the difficulties encountered the re-absorption water, there is low chemical stability of the final products.

In the next set of experiments specimens have been obtained with cement additions during mixing aqueous solutions and polymer. And in all specimens cesium have been added during solidification with the purpose to obtain data on leaching rate after the contact with water. Freshly made mixture (polymer – solution) has been mixed with cement solution in different ratios.

**Table 4.**
Results of experiments on solidification of simulated solutions with cement additives.
(Polymer # 960.)

| # | Correlation among the mass of solution, mass of polymer and mass of cement solution, % | | | Loss of weight after aging samples, during 15 days, % | Loss of weight after aging samples, during 30 days, % |
|---|---|---|---|---|---|
| | Mass of solution | Mass of polymer | Mass of cement solution | | |

| | | | | | |
|---|---|---|---|---|---|
| Solution NaOH, 0,1 M + 50 mg $Cs^+$ | | | | | |
| 1 | 78,1 | 15,6 | 6,3 | 77,1 | 79,7 |
| 2 | 69,4 | 13,9 | 16,7 | 68,5 | 69,0 |
| 3 | 41,6 | 8,4 | 50,0 | 37,9 | 55,2 |
| 4 | 27,8 | 5,6 | 66,6 | 25,6 | 33,2 |
| $H_2O$ + 50 mg $Cs^+$ | | | | | |
| 5 | 79,4 | 15,8 | 4,8 | 66,2 | 79,0 |
| 6 | 75,8 | 15,1 | 9,1 | 72,7 | 75,6 |
| 7 | 41,6 | 8,4 | 50,0 | 35,1 | 45,8 |
| 8 | 27,8 | 5,6 | 66,6 | 22,4 | 34,5 |
| Solution $HNO_3$ 0,5 M, + 50 mg $Cs^+$ | | | | | |
| 9 | 79,4 | 15,8 | 4,8 | 69,1 | 70,2 |
| 10 | 69,4 | 13,9 | 16,7 | 59,8 | 61,8 |
| 11 | 27,8 | 5,6 | 66,6 | 21,8 | 30,6 |
| Solution $HNO_3$, 5 M + 50 mg $Cs^+$ | | | | | |
| 12 | 79,4 | 15,8 | 4,8 | 45,3 | 58,2 |
| 13 | 78,1 | 15,6 | 6,3 | 46,3 | 57,8 |
| 14 | 75,8 | 15,1 | 9,1 | 44,7 | 44,5 |
| 15 | 69,4 | 13,9 | 16,7 | 41,6 | 49,5 |
| 16 | 41,6 | 8,4 | 50,0 | 25,6 | 32,2 |
| 17 | 27,8 | 5,6 | 66,6 | 19,6 | 25,2 |

After one month aging, evaporated specimens were weighed and the part of specimen (with cement) was put into a polypropylene cup with distillated water on the basis of 10 ml to 1g solid phase. After one day water was removed, the volume measured and, lastly, the content of Cs in the water was determined.

These tests were not carried out properly. The majority of specimens absorbed a large volume of water, thus utilizing # 960's full absorption capacity. Proper comparative experiments would need to include stable polymer to water bonding ratios, in other words, a bonding ratio that does not expand the absorption capacity beyond a safe limit. Consequently this data must be considered only for evaluation, but not for final conclusion. Further leach testing is necessary.

**Table 5.**
Results of chemical stability (cesium leach rate) of specimen after solidification with polymer and cement

| # | Correlation among the mass of solution, mass of polymer and mass of cement solution, % | | | The quantity of Cs, passed in water, % from the initial content in specimen |
|---|---|---|---|---|
| | Mass of solution | Mass of polymer | Mass of cement solution | |
| $H_2O$ + 50 mg $Cs^+$ | | | | |
| 8 | 27,8 | 5,6 | 66,6 | 85 |
| Solution $HNO_3$ 0,5 M, + 50 mg $Cs^{++}$ | | | | |
| 11 | 27,8 | 5,6 | 66,6 | 58 |
| Solution $HNO_3$, 5 M + 50 mg $Cs^+$ | | | | |
| 12 | 79,4 | 15,8 | 4,8 | 98 |
| 13 | 78,1 | 15,6 | 6,3 | 102 |
| 14 | 75,8 | 15,1 | 9,1 | 94 |
| 15 | 69,4 | 13,9 | 16,7 | 97 |
| 16 | 41,6 | 8,4 | 50,0 | 89 |
| 17 | 27,8 | 5,6 | 66,6 | 69 |

Preliminary experimental results indicate that alongside a number of merits in some cases, the #960 polymer alone does not ensure the achievement of certain disposal requirements in some

countries. However, it must be noted that #960 polymer is an aqueous absorbent technology and will absorb all water when in contact. It is important to note that the # 960 absorption process is mechanical one not a chemical one.

Given the disposal requirements of some countries, the simplest way to solve the leaching problem will be encapsulation (after solidification waste with polymers) in a cement matrix. As a matter of course, after adding the ample quantity of cement radionuclide leach rate should be at the level of $10^{-4} – 10^{-5}$ g/cm$^2$·day or may be less and this value will be quite justified during long-term storage. Successful cementation encapsulation has been achieved with the # 910 polymer for organic solidification in other European nations; however, economic costs remain high due to the larger cement waste form.

The challenge will be to establish a suitable technique to encapsulate the solidified waste that meets the disposal criteria for Russia. One proposal will be to add radwaste into a steel drum with polymer several times, thereby creating the immobilized form. Then mix additives to the waste form, cement or other stabilizers for example, which will result in a stable form and reduce the volume of the final waste form by 6 to 10 times, maybe more but will depend on salt content and specific gravity of the solution.

Another possibility for disposal is the incineration process. After preliminary concentration (by adding solution with polymer several times) incineration can be achieved successfully with a final waste form of ash. The ash residue after incineration can be included in proper matrix as well.

## CONCLUSIONS

The test program as outlined in this paper will provide a better understanding of the polymer technology for those participants in DOE's IPP project. Testing on actual waste streams at Seversk (SCC) and Zheleznogorsk (MCC) has commenced in December, 2009, and details of this work will be published in future papers. In addition the results of the experiments will assist the project managers with obtaining the necessary certification from ROSATOM.

Research work beyond the scope of this paper has been concluded which includes gas generation testing and the previously mentioned irradiation testing, both critically important for the validation of polymers with ILW and HLW solutions. Given the results of the first year's work on this project, it can be stated that the polymer technology is versatile and can be applied with all radioactive liquids, as well as offer significant cost savings for final storage .

It is also worth noting that the results of this work may be profitably employed for the management of high-toxic wastes generated by chemical industry plants.

In connection with aforesaid, the authors of the paper are interested in any form of cooperation with international organizations, research institutes and private companies connected with the problems radwaste and chemical waste management.

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